CENTRAL-FORCE DECOMPOSITION OF THE TERSOFF POTENTIAL

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Abstract: Central forces play important role in the analysis of results obtained with particle simulation methods, since they allow evaluating stress fields. In this work we derive expressions for a central-force decompositon of the Tersoff potential, which is often used to describe interatomic interactions in covalently bonded materials. We simplify the obtained expressions and discuss their properties.

Keywords: central-force decomposition, Tersoff potential, molecular dynamics, empirical potentials

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1. Introduction

The particle simulation methods, such as the molecular dynamics method [1–4] and the Monte Carlo method [3, 4], allow studying the behaviour of matter at the atomic level. The validity and the quality of results obtained from any atomistic simulation depends mostly on the adequacy of the potential function used to describe interatomic interactions [5, 6]. During the last 30 years an immense effort has been put into developing new empirical potentials, and many new potentials of high quality have been proposed as a result [7–16]. Among them, the Tersoff potential [17] has turned out to be one of the most successful approaches for investigating covalently bonded materials [17–27].

The overall success of the Tersoff potential mostly originates from the fact that – unlike the traditional molecular mechanics force fields – it allows the formation and dissociation of covalent chemical bonds. This is achieved by explicitly accounting for the multibody effects, which within the Tersoff potential are captured by the bond order. This parameter depends on the local chemical environment of the bond in question and acts in such a way as to control its strength. As a consequence the Tersoff potential is able to “automatically” recognize different bonding schemes, being able to simultaneously (*i.e.* within the same framework) describe single, double and triple covalent bonds. It has been recently shown that the Tersoff potential is even capable of correctly describing materials which possess mixed hybridization [28].

The analytic formulas defining the first derivatives of the Tersoff potential with respect to atomic positions are already known, since this knowledge constitutes an obligatory prerequisite for carrying out any MD simulation employing this potential. Second order derivatives (in the same sense as above) of this potential are also known [29], as they serve as the basic input for the vibrational analysis [30]. However, a more detailed analysis of the results obtained from atomistic simulations often requires also the knowledge of the potential derivatives with respect to interatomic distances. These very specific derivatives are used in calculating *e.g.* stress fields [31–33] or elastic constants [34]. In the first example the first derivatives are needed, while in the second one the knowledge of the second derivatives is required.

The above mentioned first derivatives are of particular importance, as they define the central-force decomposition (CFD) of the potential, which is a prerequisite for calculating the spatial distribution of stress within Hardy's formalism [35, 36, 33]. Finding central forces for a multibody potential is not a trivial task, as it requires a special procedure to be followed, which often involves tedious calculations. The practical onerousness of this procedure depends on the complexity of the functional form of the considered potential. These inconveniences are the reason why till now CFDs have been found only for potentials of low or moderate complexity, such as embedded atom method potentials [37], spline based modified embedded atom method potentials [33] and rather simple three-body [38] and four-body potentials [39, 40].

Although the functional form of the Tersoff potential is not very complex, to the best of our knowledge, its CFD is still unknown. As this lack hinders, or even prevents, the application of Hardy's formalism, it strongly limits the possibilities for performing – in the context of mechanics of materials – a detailed analysis of results obtained for systems described with the Tersoff potential. It is worth noting that these systems constitute a wide class of technologically important materials, ranging from bulk semiconductors (such as silicon and gallium arsenide) to nanostructures (such as fullerenes and nanotubes) and nanocrystals (such as graphene or penta-graphene). In this work we have made an attempt to fill the above mentioned gap and derive the expressions for the central-force decomposition of the Tersoff potential.

This paper is organized as follows. In Section 2 we recall the basic information about the Tersoff potential. We also remind the definition of central forces and present the overview of the method for finding central-force decomposition. In Section 3 we present the main result of this work, which is a step-by-step derivation of the expressions for the CFD for the Tersoff potential. In Section 4 we discuss the properties of the obtained decomposition. We conclude in Section 5.

2. Theoretical

2.1. Notation used

The following notation will be used throughout this work. Scalar quantities will be typed in italic and vector quantities will be denoted by bold letters. We will consider an atomic system composed of N atoms. Small indices i, j and k will be used to distinguish atoms. To denote the position vector of the i-th atom we will use vector $\mathbf{r}_i = [x_i, y_i, z_i]$. The bond vector joining atom i with atom j will be denoted with $\mathbf{r}_{ij}$, *i.e.*

$$\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i = [x_j, y_j, z_j] - [x_i, y_i, z_i] = [x_j - x_i, y_j - y_i, z_j - z_i] \tag{1}$$

Its length will be denoted with r_{ij}, *i.e.*

$$r_{ij} = \left|\mathbf{r}_{ij}\right| \tag{2}$$

The valence angle between bond vectors $\mathbf{r}_{ij}$ and $\mathbf{r}_{ik}$ will be denoted with θ_{jik}, with

$$\cos\theta_{jik} = \frac{\mathbf{r}_{ij} \cdot \mathbf{r}_{ik}}{r_{ij} r_{ik}} \tag{3}$$

The cosine rule will be often used in this paper, which for angle θ_{jik} can be written in the following form:

$$\cos\theta_{jik} = \frac{r_{ij}^2 + r_{ik}^2 - r_{jk}^2}{2 r_{ij} r_{ik}} \tag{4}$$

For the sake of brevity we shall also use

$$f'(x_0) = \left.\frac{\mathrm{d}f(x)}{\mathrm{d}x}\right|_{x_0} \tag{5}$$

to denote the first derivative of $f(x)$ evaluated at point $x = x_0$. The „×" symbol will be used in this work to denote multiplication (and *not* the cross product) in long-winded expressions, spanning several lines.

2.2. Tersoff potential

Within the Tersoff potential the total potential energy E_{tot} of the system composed of N atoms is written in the form:

$$E_{\mathrm{tot}} = \frac{1}{2} \sum_{i}^{N} \sum_{j \neq i}^{N} f_{\mathrm{C}}(r_{ij}) \left[V_{\mathrm{R}}(r_{ij}) + b_{ij} V_{\mathrm{A}}(r_{ij})\right] \tag{6}$$

with the pairwise repulsive and attractive contributions given by:

$$V_{\mathrm{R}}(r) = A \exp\left(-\lambda_1 r\right) \tag{7}$$

and

$$V_{\mathrm{A}}(r) = -B \exp\left(-\lambda_2 r\right) \tag{8}$$

Here, A, B, λ_1 and λ_2 are adjustable parameters.

The cutoff function $f_C(r)$ is defined as:

$$f_C(r)=\begin{cases}1, & \text{for } r<R-D\\ \dfrac{1}{2}-\dfrac{1}{2}\sin\left(\dfrac{\pi}{2}\dfrac{r-R}{D}\right), & \text{for } R-D\le r\le R+D\\ 0, & \text{for } r>R+D\end{cases} \tag{9}$$

and acts in such a way as to restrict the interaction range. The cutoff function smoothly cuts off the contributions from pairs of atoms, which are separated by more than $R+D$. R and D are also adjustable parameters, which specify the position and the width of the cutoff region. They are typically chosen in such a way as to include only the first coordination shell in the summation present in Equation (6).

Another summation, which is also limited by $f_C(r)$, appears in the definition of the bond order b_{ij}, which is given as:

$$b_{ij}=\left(1+\beta^n\zeta_{ij}^n\right)^{-\frac{1}{2n}} \tag{10}$$

where

$$\zeta_{ij}=\sum_{k\neq i,j}^{N} f_C(r_{ik})h(r_{ij}-r_{ik})g(\cos\theta_{jik}) \tag{11}$$

The $h(r)$ function is defined as:

$$h(r)=\exp\left(\lambda_3^m r^m\right) \tag{12}$$

Symbols β, n, λ_3 and m represent other parameters. By reason of the non-linearity present in the definition of the bond order (Equation (10)), the Tersoff potential is a many-body potential. The function $g(\cos\theta)$ describes the angular dependence and is defined as:

$$g(\cos\theta)=\gamma\left(1+\frac{c^2}{d^2}-\frac{c^2}{d^2+\left(\cos\theta-\cos\theta_0\right)^2}\right) \tag{13}$$

The angular function $g(\cos\theta)$ is determined by the parameters γ, c, d and θ_0. Therefore, fourteen parameters in total need to be specified for a single element system. There are many different parameterizations of the Tersoff potential available in the literature, mostly for elements of group IV [17–21]. However, some parameterizations for elements of groups III and V also exist [22–27].

2.3. Central-force decomposition

Knowing the potential function E_{tot} the resultant force $\mathbf{F}_i$ that acts on particle i can be always calculated using the fundamental relation:

$$\mathbf{F}_i=-\nabla_i E_{\text{tot}}=-\left[\frac{\partial}{\partial x_i},\frac{\partial}{\partial y_i},\frac{\partial}{\partial z_i}\right]E_{\text{tot}} \tag{14}$$

For pair potentials, *i.e.* the potentials which have the form:

$$E_{\text{tot}}=\frac{1}{2}\sum_{i}^{N}\sum_{j\neq i}^{N}V(r_{ij}) \tag{15}$$

the resultant force $\mathbf{F}_i$ can be written as a sum of pair interactions:

$$\mathbf{F}_i = \sum_{j \neq i}^{N} \mathbf{F}_{ij} = \sum_{j \neq i}^{N} V'(r_{ij}) \frac{\mathbf{r}_{ij}}{r_{ij}} \tag{16}$$

Here, $\mathbf{F}_{ij}$ denotes the force which is exerted on atom i by atom j. Its signed value is given by $V'(r_{ij})$ and it acts along the vector $\mathbf{r}_{ij}$, *i.e.*

$$\mathbf{F}_{ij} \parallel \mathbf{r}_{ij} \tag{17}$$

From Equation (16) it also follows that:

$$\mathbf{F}_{ji} = -\mathbf{F}_{ij} \tag{18}$$

Forces which satisfy Equations (17)–(18) are termed as central forces and play an important role in physics, as they satisfy the strong law of action and reaction.

For all pair potentials the conditions (17) and (18) are automatically met, and the total force $\mathbf{F}_i$ can be always expressed as a sum of central forces $\mathbf{F}_{ij}$. In the case of many-body potentials expressing total forces in terms of central forces is not trivial, and requires a special procedure, which is known as the central-force decomposition, to be taken. It has been shown by Admal and Tadmor [35, 36] that for potential functions of the form

$$E_{\text{tot}} = E_{\text{tot}}(r_{12}, r_{13}, \ldots, r_{1N}, r_{23}, r_{24}, \ldots, r_{2N}, \ldots, r_{N-1,N}) \tag{19}$$

i.e. the potentials which are defined on the $N(N-1)/2$ dimensional shape space

$$S: \{r_{12}, r_{13}, \ldots, r_{1N}, r_{23}, r_{24}, \ldots, r_{2N}, \ldots, r_{N-1,N}\}$$

the total force $\mathbf{F}_i$ acting on particle i can be always decomposed into central forces $\mathbf{F}_{ij}$ satisfying Equations (17)–(18), provided that the potential function (19) is continuously differentiable. As has been also shown by Admal and Tadmor [35, 36], a central-force decomposition can be obtained for such potentials by finding the derivative of the potential E_{tot} with respect to the interatomic distance r_{ij}, and is given by:

$$\mathbf{F}_{ij} = \frac{\partial E_{\text{tot}}}{\partial r_{ij}} \frac{\mathbf{r}_{ij}}{r_{ij}} \tag{20}$$

It is easy to verify that the force $\mathbf{F}_{ij}$ defined in such a way satisfies both conditions of the strong law of action and reaction (Equations (17) and (18)). Since $\mathbf{r}_{ij} = -\mathbf{r}_{ji}$ and $r_{ij} = r_{ji}$ Equation (20) can be written as:

$$\mathbf{F}_{ij} = \frac{\partial E_{\text{tot}}}{\partial r_{ij}} \frac{\mathbf{r}_{ij}}{r_{ij}} = \frac{\partial E_{\text{tot}}}{\partial r_{ji}} \frac{-\mathbf{r}_{ji}}{r_{ji}} = -\mathbf{F}_{ji} \tag{21}$$

The presence of the direction vector $\mathbf{r}_{ij}/r_{ij}$ in Equation (20) guarantees that the force $\mathbf{F}_{ij}$ is parallel to $\mathbf{r}_{ij}$.

It is worth noting that the central force defined by Equation (20) does not have to depend only on the positions of particles i and j, and in general may depend on the positions of even all particles in the system. It does not follow from the fact that the force $\mathbf{F}_{ij}$ is not expressible as a function of only r_{ij} that the considered potential is not decomposable into central forces.

3. Deriving CFD for the Tersoff potential

In this section we derive the expression for the first derivative of the Tersoff potential (defined by Equations (6)–(13)) with respect to the interatomic distance, *i.e.* $\partial E_{\mathrm{tot}}/\partial r_{\alpha\beta}$. The central forces can then be obtained using Equation (20).

We start our derivation by differentiating E_{tot} with respect to $r_{\alpha\beta}$:

$$\begin{aligned}\frac{\partial E_{\mathrm{tot}}}{\partial r_{\alpha\beta}} &= \frac{\partial}{\partial r_{\alpha\beta}}\left(\frac{1}{2}\sum_{i}^{N}\sum_{j\neq i}^{N} f_{\mathrm{C}}(r_{ij})\left[V_{\mathrm{R}}(r_{ij})+b_{ij}V_{\mathrm{A}}(r_{ij})\right]\right)\\
&= \frac{1}{2}\sum_{i}^{N}\sum_{j\neq i}^{N}\frac{\partial f_{\mathrm{C}}(r_{ij})}{\partial r_{\alpha\beta}}\left[V_{\mathrm{R}}(r_{ij})+b_{ij}V_{\mathrm{A}}(r_{ij})\right]+\\
&\quad \frac{1}{2}\sum_{i}^{N}\sum_{j\neq i}^{N} f_{\mathrm{C}}(r_{ij})\left[\frac{\partial V_{\mathrm{R}}(r_{ij})}{\partial r_{\alpha\beta}}+\frac{\partial b_{ij}}{\partial r_{\alpha\beta}}V_{\mathrm{A}}(r_{ij})+b_{ij}\frac{\partial V_{\mathrm{A}}(r_{ij})}{\partial r_{\alpha\beta}}\right]\\
&= \frac{1}{2}\sum_{i}^{N}\sum_{j\neq i}^{N} f_{\mathrm{C}}'(r_{ij})\left[V_{\mathrm{R}}(r_{ij})+b_{ij}V_{\mathrm{A}}(r_{ij})\right]\frac{\partial r_{ij}}{\partial r_{\alpha\beta}}+\\
&\quad \frac{1}{2}\sum_{i}^{N}\sum_{j\neq i}^{N} f_{\mathrm{C}}(r_{ij})\left[V_{\mathrm{R}}'(r_{ij})+b_{ij}V_{\mathrm{A}}'(r_{ij})\right]\frac{\partial r_{ij}}{\partial r_{\alpha\beta}}+\\
&\quad \frac{1}{2}\sum_{i}^{N}\sum_{j\neq i}^{N} f_{\mathrm{C}}(r_{ij})\frac{\partial b_{ij}}{\partial r_{\alpha\beta}}V_{\mathrm{A}}(r_{ij})\\
&= A_1+A_2+A_3\end{aligned}\tag{22}$$

Here, we apply the chain rule, *i.e.*

$$\frac{\partial f(r_{ij})}{\partial r_{\alpha\beta}} = f'(r_{ij})\frac{\partial r_{ij}}{\partial r_{\alpha\beta}}\tag{23}$$

when moving to the final form. We also employ a short notation of Equation (5). We have also introduced symbols A_1, A_2 A_3 which represent three terms of the final form of Equation (23). In order to facilitate further derivation we will handle each of the $A_1 - A_3$ terms separately.

Using the Kronecker delta δ_{ij} the derivative $\partial r_{ij}/\partial r_{\alpha\beta}$ can be written as:

$$\frac{\partial r_{ij}}{\partial r_{\alpha\beta}} = \delta_{i\alpha}\delta_{j\beta}+\delta_{i\beta}\delta_{j\alpha}\tag{24}$$

This allows us to write A_1 as:

$$\begin{aligned}A_1 &= \frac{1}{2}\sum_{i}^{N}\sum_{j\neq i}^{N} f_{\mathrm{C}}'(r_{ij})\left[V_{\mathrm{R}}(r_{ij})+b_{ij}V_{\mathrm{A}}(r_{ij})\right]\frac{\partial r_{ij}}{\partial r_{\alpha\beta}}\\
&= \frac{1}{2}\sum_{i}^{N}\sum_{j\neq i}^{N} f_{\mathrm{C}}'(r_{ij})\left[V_{\mathrm{R}}(r_{ij})+b_{ij}V_{\mathrm{A}}(r_{ij})\right]\left(\delta_{i\alpha}\delta_{j\beta}+\delta_{i\beta}\delta_{j\alpha}\right)\end{aligned}\tag{25}$$

which accounting for the Kronecker deltas reduces to:

$$A_1 = f_{\mathrm{C}}'(r_{\alpha\beta})\left[V_{\mathrm{R}}(r_{\alpha\beta})+\frac{b_{\alpha\beta}+b_{\beta\alpha}}{2}V_{\mathrm{A}}(r_{\alpha\beta})\right]\tag{26}$$

We remind that

$$b_{\alpha\beta} \neq b_{\beta\alpha} \tag{27}$$

because of the definition of the bond order (see Equations (10)–(13)). A similar procedure can be applied in order to simplify A_2, for which we obtain:

$$\begin{aligned} A_2 &= \frac{1}{2}\sum_{i}^{N}\sum_{j\neq i}^{N} f_{\mathrm{C}}(r_{ij})\left[V_{\mathrm{R}}'(r_{ij}) + b_{ij}V_{\mathrm{A}}'(r_{ij})\right]\frac{\partial r_{ij}}{\partial r_{\alpha\beta}} \\ &= \frac{1}{2}\sum_{i}^{N}\sum_{j\neq i}^{N} f_{\mathrm{C}}(r_{ij})\left[V_{\mathrm{R}}'(r_{ij}) + b_{ij}V_{\mathrm{A}}'(r_{ij})\right]\left(\delta_{i\alpha}\delta_{j\beta} + \delta_{i\beta}\delta_{j\alpha}\right) \\ &= f_{\mathrm{C}}(r_{\alpha\beta})\left[V_{\mathrm{R}}'(r_{\alpha\beta}) + \frac{b_{\alpha\beta}+b_{\beta\alpha}}{2}V_{\mathrm{A}}'(r_{\alpha\beta})\right] \end{aligned} \tag{28}$$

Now we find the derivatives $f_{\mathrm{C}}'(r)$, $V_{\mathrm{R}}'(r)$ and $V_{\mathrm{A}}'(r)$ which appear in the final forms of A_1 and A_2.

For the cutoff function $f_{\mathrm{C}}(r)$ we obtain:

$$f_{\mathrm{C}}'(r) = \begin{cases} -\dfrac{\pi}{4D}\cos\left(\dfrac{\pi}{2}\dfrac{r-R}{D}\right), & \text{for} \quad R-D \le r \le R+D \\ 0, & \text{otherwise} \end{cases} \tag{29}$$

For the repulsive term $V_{\mathrm{R}}(r)$ we get:

$$V_{\mathrm{R}}'(r) = -\lambda_1 A \exp\left(-\lambda_1 r\right) \tag{30}$$

and for the attractive term $V_{\mathrm{A}}(r)$ we get:

$$V_{\mathrm{A}}'(r) = \lambda_2 B \exp\left(-\lambda_2 r\right) \tag{31}$$

Now we can proceed with the last term A_3 which is the most complex among $A_1 - A_3$.

We start with the derivative of the bond order b_{ij}. By differentiating Equation (10) and applying the chain rule we obtain:

$$\frac{\partial b_{ij}}{\partial r_{\alpha\beta}} = \frac{\partial b_{ij}}{\partial \zeta_{ij}}\frac{\partial \zeta_{ij}}{\partial r_{\alpha\beta}} = b_{ij}'\frac{\partial \zeta_{ij}}{\partial r_{\alpha\beta}} \tag{32}$$

where

$$\begin{aligned} b_{ij}' &= \frac{\partial b_{ij}}{\partial \zeta_{ij}} = \frac{\partial}{\partial \zeta_{ij}}\left(\left(1+\beta^n\zeta_{ij}^n\right)^{-\frac{1}{2n}}\right) \\ &= -\frac{1}{2n}\left(1+\beta^n\zeta_{ij}^n\right)^{-\frac{1}{2n}-1}\beta^n n\zeta_{ij}^{n-1} \\ &= -\frac{\beta^n}{2}\left(1+\beta^n\zeta_{ij}^n\right)^{-\frac{1+2n}{2n}}\zeta_{ij}^{n-1} \end{aligned} \tag{33}$$

By plugging this result into the expression for A_3 we obtain:

$$\begin{aligned} A_3 &= \frac{1}{2}\sum_{i}^{N}\sum_{j\neq i}^{N} f_{\mathrm{C}}(r_{ij})\frac{\partial b_{ij}}{\partial r_{\alpha\beta}}V_{\mathrm{A}}(r_{ij}) \\ &= \frac{1}{2}\sum_{i}^{N}\sum_{j\neq i}^{N} f_{\mathrm{C}}(r_{ij})b_{ij}'\frac{\partial \zeta_{ij}}{\partial r_{\alpha\beta}}V_{\mathrm{A}}(r_{ij}) \end{aligned} \tag{34}$$

Now we need to find the derivative of the ζ_{ij} term.

Accounting for its definition we obtain:

$$\begin{aligned}\frac{\partial \zeta_{ij}}{\partial r_{\alpha\beta}} &= \frac{\partial}{\partial r_{\alpha\beta}}\left(\sum_{k\neq i,j}^{N} f_{\mathrm{C}}(r_{ik})h(r_{ij}-r_{ik})g(\cos\theta_{jik})\right)\\ &= \sum_{k\neq i,j}^{N}\left[\frac{\partial f_{\mathrm{C}}(r_{ik})}{\partial r_{\alpha\beta}}h(r_{ij}-r_{ik})g(\cos\theta_{jik})+\right.\\ &\qquad f_{\mathrm{C}}(r_{ik})\frac{\partial h(r_{ij}-r_{ik})}{\partial r_{\alpha\beta}}g(\cos\theta_{jik})+\\ &\qquad \left. f_{\mathrm{C}}(r_{ik})h(r_{ij}-r_{ik})\frac{\partial g(\cos\theta_{jik})}{\partial r_{\alpha\beta}}\right]\end{aligned} \tag{35}$$

Using the chain rule once again this can be written as:

$$\begin{aligned}\frac{\partial \zeta_{ij}}{\partial r_{\alpha\beta}} &= \sum_{k\neq i,j}^{N}\left[f'_{\mathrm{C}}(r_{ik})\frac{\partial r_{ik}}{\partial r_{\alpha\beta}}h(r_{ij}-r_{ik})g(\cos\theta_{jik})+\right.\\ &\qquad f_{\mathrm{C}}(r_{ik})h'(r_{ij}-r_{ik})\frac{\partial (r_{ij}-r_{ik})}{\partial r_{\alpha\beta}}g(\cos\theta_{jik})+\\ &\qquad \left. f_{\mathrm{C}}(r_{ik})h(r_{ij}-r_{ik})g'(\cos\theta_{jik})\frac{\partial \cos\theta_{jik}}{\partial r_{\alpha\beta}}\right]\\ &= B_1+B_2+B_3\end{aligned} \tag{36}$$

where the derivative of the $h(r)$ function (defined by Equation (12)) is given as:

$$h'(r) = \lambda_3^m m r^{m-1}\exp\left(\lambda_3^m r^m\right) \tag{37}$$

and the derivative $g'(\cos\theta)$, found by differentiating Equation (13), can be expressed as:

$$g'(\cos\theta) = \frac{2\gamma c^2(\cos\theta-\cos\theta_0)}{\left[d^2+(\cos\theta-\cos\theta_0)^2\right]^2} \tag{38}$$

In Equation (36) once again we have introduced new symbols (B_1, B_2 and B_3) to denote three sums present. For the sake of clarity we will elaborate them separately.

We start with the sum B_1 which accounting for Equation (24) will take the following form:

$$\begin{aligned}B_1 &= \sum_{k\neq i,j}^{N} f'_{\mathrm{C}}(r_{ik})\frac{\partial r_{ik}}{\partial r_{\alpha\beta}}h(r_{ij}-r_{ik})g(\cos\theta_{jik})\\ &= \sum_{k\neq i,j}^{N}\left(\delta_{i\alpha}\delta_{k\beta}+\delta_{i\beta}\delta_{k\alpha}\right)f'_{\mathrm{C}}(r_{ik})h(r_{ij}-r_{ik})g(\cos\theta_{jik})\\ &= \sum_{k\neq i,j}^{N}\delta_{i\alpha}\delta_{k\beta}f'_{\mathrm{C}}(r_{ik})h(r_{ij}-r_{ik})g(\cos\theta_{jik})+\\ &\qquad \sum_{k\neq i,j}^{N}\delta_{i\beta}\delta_{k\alpha}f'_{\mathrm{C}}(r_{ik})h(r_{ij}-r_{ik})g(\cos\theta_{jik})\end{aligned} \tag{39}$$

$$= B_{1,1} + B_{1,2}$$

Here, once again we have introduced additional symbols, to simplify further presentation.

Now we move to the sum B_2, which is given as:

$$B_2 = \sum_{k \neq i,j}^{N} f_{\mathrm{C}}(r_{ik}) h'(r_{ij} - r_{ik}) \frac{\partial(r_{ij} - r_{ik})}{\partial r_{\alpha\beta}} g(\cos\theta_{jik}) \tag{40}$$

By using Equation (24) the derivative $\partial(r_{ij} - r_{ik})/\partial r_{\alpha\beta}$ can be expressed as:

$$\frac{\partial(r_{ij} - r_{ik})}{\partial r_{\alpha\beta}} = \frac{\partial r_{ij}}{\partial r_{\alpha\beta}} - \frac{\partial r_{ik}}{\partial r_{\alpha\beta}} = \delta_{i\alpha}\delta_{j\beta} + \delta_{i\beta}\delta_{j\alpha} - \left(\delta_{i\alpha}\delta_{k\beta} + \delta_{i\beta}\delta_{k\alpha}\right) \tag{41}$$

which allows us to write B_2 as:

$$\begin{aligned} B_2 = & \sum_{k \neq i,j}^{N} \delta_{i\alpha}\delta_{j\beta} f_{\mathrm{C}}(r_{ik}) h'(r_{ij} - r_{ik}) g(\cos\theta_{jik}) + \\ & \sum_{k \neq i,j}^{N} \delta_{i\beta}\delta_{j\alpha} f_{\mathrm{C}}(r_{ik}) h'(r_{ij} - r_{ik}) g(\cos\theta_{jik}) - \\ & \sum_{k \neq i,j}^{N} \delta_{i\alpha}\delta_{k\beta} f_{\mathrm{C}}(r_{ik}) h'(r_{ij} - r_{ik}) g(\cos\theta_{jik}) - \\ & \sum_{k \neq i,j}^{N} \delta_{i\beta}\delta_{k\alpha} f_{\mathrm{C}}(r_{ik}) h'(r_{ij} - r_{ik}) g(\cos\theta_{jik}) \\ = & B_{2,1} + B_{2,2} + B_{2,3} + B_{2,4} \end{aligned} \tag{42}$$

Here, once again we have introduced new symbols, which represent four sums that appear in B_2.

Elaboration of the last term of Equation (36), *i.e.* the sum B_3, requires knowing the derivative $\partial\cos\theta_{jik}/\partial r_{\alpha\beta}$. As the angle θ_{jik} can depend on $r_{\alpha\beta}$ in six ways (through $\theta_{\beta\alpha k}$, $\theta_{\alpha\beta k}$, $\theta_{j\alpha\beta}$, and $\theta_{j\beta\alpha}$; through $\theta_{\alpha i\beta}$, $\theta_{\beta i\alpha}$), the derivative $\partial\cos\theta_{jik}/\partial r_{\alpha\beta}$ can be written as:

$$\begin{aligned} \frac{\partial\cos\theta_{jik}}{\partial r_{\alpha\beta}} = & (\delta_{i\alpha}\delta_{j\beta} + \delta_{i\beta}\delta_{j\alpha}) \frac{\partial\cos\theta_{jik}}{\partial r_{ij}} + \\ & (\delta_{i\alpha}\delta_{k\beta} + \delta_{i\beta}\delta_{k\alpha}) \frac{\partial\cos\theta_{jik}}{\partial r_{ik}} + \\ & (\delta_{j\alpha}\delta_{k\beta} + \delta_{j\beta}\delta_{k\alpha}) \frac{\partial\cos\theta_{jik}}{\partial r_{jk}} \end{aligned} \tag{43}$$

Here, we have used the fact that $r_{ij} = r_{ji}$, and thus $\partial\cos\theta_{jik}/\partial r_{ij} = \partial\cos\theta_{jik}/\partial r_{ji}$. Three derivatives required in Equation (43), *i.e.* $\partial\cos\theta_{jik}/\partial r_{ij}$, $\partial\cos\theta_{jik}/\partial r_{ik}$ and

$\partial\cos\theta_{jik}/\partial r_{jk}$, can be found using the cosine rule. By differentiating Equation (4) we obtain:

$$\frac{\partial\cos\theta_{jik}}{\partial r_{ij}} = \frac{\cos\theta_{jik}}{r_{ij}} - \frac{r_{ik}^2 - r_{jk}^2}{r_{ik}}\frac{1}{r_{ij}^2} \tag{44}$$

$$\frac{\partial\cos\theta_{jik}}{\partial r_{ik}} = \frac{\cos\theta_{jik}}{r_{ik}} - \frac{r_{ij}^2 - r_{jk}^2}{r_{ij}}\frac{1}{r_{ik}^2} \tag{45}$$

and

$$\frac{\partial\cos\theta_{jik}}{\partial r_{jk}} = -\frac{r_{jk}}{r_{ij}r_{ik}} \tag{46}$$

We note that after performing the differentiation we need to employ the cosine rule and identify the resultant terms, in order to obtain the final forms presented above. By combining (44), (45) and (46) with (43) the final expression for the derivative $\partial\cos\theta_{jik}/\partial r_{\alpha\beta}$ is obtained:

$$\begin{aligned}\frac{\partial\cos\theta_{jik}}{\partial r_{\alpha\beta}} = {} & (\delta_{i\alpha}\delta_{j\beta} + \delta_{i\beta}\delta_{j\alpha})\left[\frac{\cos\theta_{jik}}{r_{ij}} - \frac{r_{ik}^2 - r_{jk}^2}{r_{ik}}\frac{1}{r_{ij}^2}\right] + \\ & (\delta_{i\alpha}\delta_{k\beta} + \delta_{i\beta}\delta_{k\alpha})\left[\frac{\cos\theta_{jik}}{r_{ik}} - \frac{r_{ij}^2 - r_{jk}^2}{r_{ij}}\frac{1}{r_{ik}^2}\right] - \\ & (\delta_{j\alpha}\delta_{k\beta} + \delta_{j\beta}\delta_{k\alpha})\frac{r_{jk}}{r_{ij}r_{ik}}\end{aligned} \tag{47}$$

Now once we have $\partial\cos\theta_{jik}/\partial r_{\alpha\beta}$ we can return to the B_3 term, which – after plugging Equation (47) into its definition (Equation (36)) – will be given as a sum of the ten terms:

$$B_3 = B_{3,1} + B_{3,2} + B_{3,3} + B_{3,4} + B_{3,5} + B_{3,6} + B_{3,7} + B_{3,8} + B_{3,9} + B_{3,10} \tag{48}$$

where:

$$B_{3,1} = \sum_{k\neq i,j}^{N} \delta_{i\alpha}\delta_{j\beta} f_{\mathrm{C}}(r_{ik}) h(r_{ij} - r_{ik}) g'(\cos\theta_{jik}) \frac{\cos\theta_{jik}}{r_{ij}} \tag{49}$$

$$B_{3,2} = -\sum_{k\neq i,j}^{N} \delta_{i\alpha}\delta_{j\beta} f_{\mathrm{C}}(r_{ik}) h(r_{ij} - r_{ik}) g'(\cos\theta_{jik}) \frac{r_{ik}^2 - r_{jk}^2}{r_{ik}}\frac{1}{r_{ij}^2} \tag{50}$$

$$B_{3,3} = \sum_{k\neq i,j}^{N} \delta_{i\beta}\delta_{j\alpha} f_{\mathrm{C}}(r_{ik}) h(r_{ij} - r_{ik}) g'(\cos\theta_{jik}) \frac{\cos\theta_{jik}}{r_{ij}} \tag{51}$$

$$B_{3,4} = -\sum_{k\neq i,j}^{N} \delta_{i\beta}\delta_{j\alpha} f_{\mathrm{C}}(r_{ik}) h(r_{ij} - r_{ik}) g'(\cos\theta_{jik}) \frac{r_{ik}^2 - r_{jk}^2}{r_{ik}}\frac{1}{r_{ij}^2} \tag{52}$$

$$B_{3,5} = \sum_{k\neq i,j}^{N} \delta_{i\alpha}\delta_{k\beta} f_{\mathrm{C}}(r_{ik}) h(r_{ij} - r_{ik}) g'(\cos\theta_{jik}) \frac{\cos\theta_{jik}}{r_{ik}} \tag{53}$$

$$B_{3,6} = -\sum_{k\neq i,j}^{N} \delta_{i\alpha}\delta_{k\beta} f_{\mathrm{C}}(r_{ik}) h(r_{ij} - r_{ik}) g'(\cos\theta_{jik}) \frac{r_{ij}^2 - r_{jk}^2}{r_{ij}}\frac{1}{r_{ik}^2} \tag{54}$$

$$B_{3,7} = \sum_{k\neq i,j}^{N} \delta_{i\beta}\delta_{k\alpha} f_{\mathrm{C}}(r_{ik}) h(r_{ij}-r_{ik}) g'(\cos\theta_{jik}) \frac{\cos\theta_{jik}}{r_{ik}} \tag{55}$$

$$B_{3,8} = -\sum_{k\neq i,j}^{N} \delta_{i\beta}\delta_{k\alpha} f_{\mathrm{C}}(r_{ik}) h(r_{ij}-r_{ik}) g'(\cos\theta_{jik}) \frac{r_{ij}^2-r_{jk}^2}{r_{ij}} \frac{1}{r_{ik}^2} \tag{56}$$

$$B_{3,9} = -\sum_{k\neq i,j}^{N} \delta_{j\alpha}\delta_{k\beta} f_{\mathrm{C}}(r_{ik}) h(r_{ij}-r_{ik}) g'(\cos\theta_{jik}) \frac{r_{jk}}{r_{ij}r_{ik}} \tag{57}$$

$$B_{3,10} = -\sum_{k\neq i,j}^{N} \delta_{j\beta}\delta_{k\alpha} f_{\mathrm{C}}(r_{ik}) h(r_{ij}-r_{ik}) g'(\cos\theta_{jik}) \frac{r_{jk}}{r_{ij}r_{ik}} \tag{58}$$

Now, once we have expanded all the terms in the expression for $\partial\zeta_{ij}/\partial r_{\alpha\beta}$ (see Equation (34)) we are ready to go back to Equation (29) and elaborate the expression for A_3. It will be composed of sixteen terms, because B_1, B_2 and B_3 are composed of two, four and ten terms, respectively. The expression for A_3 was (compare with Equation (34)):

$$A_3 = \frac{1}{2}\sum_{i}^{N}\sum_{j\neq i}^{N} f_{\mathrm{C}}(r_{ij}) b'_{ij} \frac{\partial\zeta_{ij}}{\partial r_{\alpha\beta}} V_{\mathrm{A}}(r_{ij}) \tag{59}$$

which after plugging formulas for B_1, B_2 and B_3 (see Equations (39), (42) and (48), respectively) will read:

$$\begin{aligned} A_3 = \frac{1}{2}\sum_{i}^{N}\sum_{j\neq i}^{N} f_{\mathrm{C}}(r_{ij}) b'_{ij} V_{\mathrm{A}}(r_{ij}) \times \Big(& B_{1,1}+B_{1,2}+B_{2,1}+B_{2,2}+B_{2,3}+B_{2,4}+ \\ & B_{3,1}+B_{3,2}+B_{3,3}+B_{3,4}+B_{3,5}+B_{3,6}+B_{3,7}+B_{3,8}+B_{3,9}+B_{3,10}\Big) \\ = \frac{1}{2}\Big(C_{3,1}+C_{3,2}+\ldots+C_{3,16}\Big) & \end{aligned} \tag{60}$$

Now, we will separately elaborate each of the sixteen triple sums which originate from this expression.

We start with $C_{3,1}$, which is given as:

$$\begin{aligned} C_{3,1} &= \sum_{i}^{N}\sum_{j\neq i}^{N} f_{\mathrm{C}}(r_{ij}) b'_{ij} V_{\mathrm{A}}(r_{ij}) \sum_{k\neq i,j}^{N} \delta_{i\alpha}\delta_{k\beta} f'_{\mathrm{C}}(r_{ik}) h(r_{ij}-r_{ik}) g(\cos\theta_{jik}) \\ &= \sum_{j\neq\alpha,\beta}^{N} f_{\mathrm{C}}(r_{\alpha j}) b'_{\alpha j} V_{\mathrm{A}}(r_{\alpha j}) f'_{\mathrm{C}}(r_{\alpha\beta}) h(r_{\alpha j}-r_{\alpha\beta}) g(\cos\theta_{j\alpha\beta}) \\ &= f'_{\mathrm{C}}(r_{\alpha\beta}) \sum_{j\neq\alpha,\beta}^{N} f_{\mathrm{C}}(r_{\alpha j}) b'_{\alpha j} V_{\mathrm{A}}(r_{\alpha j}) h(r_{\alpha j}-r_{\alpha\beta}) g(\cos\theta_{j\alpha\beta}) \\ &= f'_{\mathrm{C}}(r_{\alpha\beta}) \sum_{i\neq\alpha,\beta}^{N} f_{\mathrm{C}}(r_{\alpha i}) b'_{\alpha i} V_{\mathrm{A}}(r_{\alpha i}) h(r_{\alpha i}-r_{\alpha\beta}) g(\cos\theta_{i\alpha\beta}) \end{aligned} \tag{61}$$

The final form was obtained by accounting for the Kronecker deltas. We also renamed dummy indices so that only α, β and i remained. We will use this convention consequently. We process $C_{3,2}$ in a similar way:

$$\begin{aligned}C_{3,2} &= \sum_{i}^{N}\sum_{j\neq i}^{N} f_{\mathrm{C}}(r_{ij}) b'_{ij} V_{\mathrm{A}}(r_{ij}) \sum_{k\neq i,j}^{N} \delta_{i\beta}\delta_{k\alpha} f'_{\mathrm{C}}(r_{ik}) h(r_{ij}-r_{ik}) g(\cos\theta_{jik}) \\ &= \sum_{j\neq\beta,\alpha}^{N} f_{\mathrm{C}}(r_{\beta j}) b'_{\beta j} V_{\mathrm{A}}(r_{\beta j}) f'_{\mathrm{C}}(r_{\beta\alpha}) h(r_{\beta j}-r_{\beta\alpha}) g(\cos\theta_{j\beta\alpha}) \\ &= f'_{\mathrm{C}}(r_{\beta\alpha}) \sum_{j\neq\beta,\alpha}^{N} f_{\mathrm{C}}(r_{\beta j}) b'_{\beta j} V_{\mathrm{A}}(r_{\beta j}) h(r_{\beta j}-r_{\beta\alpha}) g(\cos\theta_{j\beta\alpha}) \\ &= f'_{\mathrm{C}}(r_{\beta\alpha}) \sum_{i\neq\beta,\alpha}^{N} f_{\mathrm{C}}(r_{\beta i}) b'_{\beta i} V_{\mathrm{A}}(r_{\beta i}) h(r_{\beta i}-r_{\beta\alpha}) g(\cos\theta_{i\beta\alpha})\end{aligned} \tag{62}$$

The next four terms, which correspond to B_2, will be given as:

$$\begin{aligned}C_{3,3} &= \sum_{i}^{N}\sum_{j\neq i}^{N} f_{\mathrm{C}}(r_{ij}) b'_{ij} V_{\mathrm{A}}(r_{ij}) \sum_{k\neq i,j}^{N} \delta_{i\alpha}\delta_{j\beta} f_{\mathrm{C}}(r_{ik}) h'(r_{ij}-r_{ik}) g(\cos\theta_{jik}) \\ &= f_{\mathrm{C}}(r_{\alpha\beta}) b'_{\alpha\beta} V_{\mathrm{A}}(r_{\alpha\beta}) \sum_{k\neq\alpha,\beta}^{N} f_{\mathrm{C}}(r_{\alpha k}) h'(r_{\alpha\beta}-r_{\alpha k}) g(\cos\theta_{\beta\alpha k}) \\ &= f_{\mathrm{C}}(r_{\alpha\beta}) b'_{\alpha\beta} V_{\mathrm{A}}(r_{\alpha\beta}) \sum_{i\neq\alpha,\beta}^{N} f_{\mathrm{C}}(r_{\alpha i}) h'(r_{\alpha\beta}-r_{\alpha i}) g(\cos\theta_{\beta\alpha i})\end{aligned} \tag{63}$$

$$\begin{aligned}C_{3,4} &= \sum_{i}^{N}\sum_{j\neq i}^{N} f_{\mathrm{C}}(r_{ij}) b'_{ij} V_{\mathrm{A}}(r_{ij}) \sum_{k\neq i,j}^{N} \delta_{i\beta}\delta_{j\alpha} f_{\mathrm{C}}(r_{ik}) h'(r_{ij}-r_{ik}) g(\cos\theta_{jik}) \\ &= f_{\mathrm{C}}(r_{\beta\alpha}) b'_{\beta\alpha} V_{\mathrm{A}}(r_{\beta\alpha}) \sum_{k\neq\beta,\alpha}^{N} f_{\mathrm{C}}(r_{\beta k}) h'(r_{\beta\alpha}-r_{\beta k}) g(\cos\theta_{\alpha\beta k}) \\ &= f_{\mathrm{C}}(r_{\beta\alpha}) b'_{\beta\alpha} V_{\mathrm{A}}(r_{\beta\alpha}) \sum_{i\neq\beta,\alpha}^{N} f_{\mathrm{C}}(r_{\beta i}) h'(r_{\beta\alpha}-r_{\beta i}) g(\cos\theta_{\alpha\beta i})\end{aligned} \tag{64}$$

$$\begin{aligned}C_{3,5} &= -\sum_{i}^{N}\sum_{j\neq i}^{N} f_{\mathrm{C}}(r_{ij}) b'_{ij} V_{\mathrm{A}}(r_{ij}) \sum_{k\neq i,j}^{N} \delta_{i\alpha}\delta_{k\beta} f_{\mathrm{C}}(r_{ik}) h'(r_{ij}-r_{ik}) g(\cos\theta_{jik}) \\ &= -\sum_{j\neq\alpha,\beta}^{N} f_{\mathrm{C}}(r_{\alpha j}) b'_{\alpha j} V_{\mathrm{A}}(r_{\alpha j}) f_{\mathrm{C}}(r_{\alpha\beta}) h'(r_{\alpha j}-r_{\alpha\beta}) g(\cos\theta_{j\alpha\beta}) \\ &= -f_{\mathrm{C}}(r_{\alpha\beta}) \sum_{i\neq\alpha,\beta}^{N} f_{\mathrm{C}}(r_{\alpha i}) b'_{\alpha i} V_{\mathrm{A}}(r_{\alpha i}) h'(r_{\alpha i}-r_{\alpha\beta}) g(\cos\theta_{i\alpha\beta})\end{aligned} \tag{65}$$

and

$$\begin{aligned}C_{3,6} &= -\sum_{i}^{N}\sum_{j\neq i}^{N} f_{\mathrm{C}}(r_{ij}) b'_{ij} V_{\mathrm{A}}(r_{ij}) \sum_{k\neq i,j}^{N} \delta_{i\beta}\delta_{k\alpha} f_{\mathrm{C}}(r_{ik}) h'(r_{ij}-r_{ik}) g(\cos\theta_{jik}) \\ &= -\sum_{j\neq\beta,\alpha}^{N} f_{\mathrm{C}}(r_{\beta j}) b'_{\beta j} V_{\mathrm{A}}(r_{\beta j}) f_{\mathrm{C}}(r_{\beta\alpha}) h'(r_{\beta j}-r_{\beta\alpha}) g(\cos\theta_{j\beta\alpha})\end{aligned} \tag{66}$$

$$=-f_{\mathrm{C}}(r_{\beta\alpha})\sum_{i\neq\beta,\alpha}^{N}f_{\mathrm{C}}(r_{\beta i})b'_{\beta i}V_{\mathrm{A}}(r_{\beta i})h'(r_{\beta i}-r_{\beta\alpha})g(\cos\theta_{i\beta\alpha})$$

Now we will elaborate terms which originate from B_3, *i.e.* $C_{3,7}$–$C_{3,16}$. They are given as:

$$\begin{aligned}C_{3,7}&=\sum_{i}^{N}\sum_{j\neq i}^{N}f_{\mathrm{C}}(r_{ij})b'_{ij}V_{\mathrm{A}}(r_{ij})\sum_{k\neq i,j}^{N}\delta_{i\alpha}\delta_{j\beta}f_{\mathrm{C}}(r_{ik})h(r_{ij}-r_{ik})g'(\cos\theta_{jik})\frac{\cos\theta_{jik}}{r_{ij}}\\&=\frac{f_{\mathrm{C}}(r_{\alpha\beta})}{r_{\alpha\beta}}b'_{\alpha\beta}V_{\mathrm{A}}(r_{\alpha\beta})\sum_{k\neq\alpha,\beta}^{N}f_{\mathrm{C}}(r_{\alpha k})h(r_{\alpha\beta}-r_{\alpha k})g'(\cos\theta_{\beta\alpha k})\cos\theta_{\beta\alpha k}\\&=\frac{f_{\mathrm{C}}(r_{\alpha\beta})}{r_{\alpha\beta}}b'_{\alpha\beta}V_{\mathrm{A}}(r_{\alpha\beta})\sum_{i\neq\alpha,\beta}^{N}f_{\mathrm{C}}(r_{\alpha i})h(r_{\alpha\beta}-r_{\alpha i})g'(\cos\theta_{\beta\alpha i})\cos\theta_{\beta\alpha i}\end{aligned}\tag{67}$$

$$\begin{aligned}C_{3,8}&=-\sum_{i}^{N}\sum_{j\neq i}^{N}f_{\mathrm{C}}(r_{ij})b'_{ij}V_{\mathrm{A}}(r_{ij})\sum_{k\neq i,j}^{N}\delta_{i\alpha}\delta_{j\beta}f_{\mathrm{C}}(r_{ik})h(r_{ij}-r_{ik})g'(\cos\theta_{jik})\frac{r_{ik}^2-r_{jk}^2}{r_{ik}}\frac{1}{r_{ij}^2}\\&=-\frac{f_{\mathrm{C}}(r_{\alpha\beta})}{r_{\alpha\beta}^2}b'_{\alpha\beta}V_{\mathrm{A}}(r_{\alpha\beta})\sum_{k\neq\alpha,\beta}^{N}f_{\mathrm{C}}(r_{\alpha k})h(r_{\alpha\beta}-r_{\alpha k})g'(\cos\theta_{\beta\alpha k})\frac{r_{\alpha k}^2-r_{\beta k}^2}{r_{\alpha k}}\\&=-\frac{f_{\mathrm{C}}(r_{\alpha\beta})}{r_{\alpha\beta}^2}b'_{\alpha\beta}V_{\mathrm{A}}(r_{\alpha\beta})\sum_{i\neq\alpha,\beta}^{N}f_{\mathrm{C}}(r_{\alpha i})h(r_{\alpha\beta}-r_{\alpha i})g'(\cos\theta_{\beta\alpha i})\frac{r_{\alpha i}^2-r_{\beta i}^2}{r_{\alpha i}}\end{aligned}\tag{68}$$

$$\begin{aligned}C_{3,9}&=\sum_{i}^{N}\sum_{j\neq i}^{N}f_{\mathrm{C}}(r_{ij})b'_{ij}V_{\mathrm{A}}(r_{ij})\sum_{k\neq i,j}^{N}\delta_{i\beta}\delta_{j\alpha}f_{\mathrm{C}}(r_{ik})h(r_{ij}-r_{ik})g'(\cos\theta_{jik})\frac{\cos\theta_{jik}}{r_{ij}}\\&=\frac{f_{\mathrm{C}}(r_{\beta\alpha})}{r_{\beta\alpha}}b'_{\beta\alpha}V_{\mathrm{A}}(r_{\beta\alpha})\sum_{k\neq\beta,\alpha}^{N}f_{\mathrm{C}}(r_{\beta k})h(r_{\beta\alpha}-r_{\beta k})g'(\cos\theta_{\alpha\beta k})\cos\theta_{\alpha\beta k}\\&=\frac{f_{\mathrm{C}}(r_{\beta\alpha})}{r_{\beta\alpha}}b'_{\beta\alpha}V_{\mathrm{A}}(r_{\beta\alpha})\sum_{i\neq\beta,\alpha}^{N}f_{\mathrm{C}}(r_{\beta i})h(r_{\beta\alpha}-r_{\beta i})g'(\cos\theta_{\alpha\beta i})\cos\theta_{\alpha\beta i}\end{aligned}\tag{69}$$

$$\begin{aligned}C_{3,10}&=-\sum_{i}^{N}\sum_{j\neq i}^{N}f_{\mathrm{C}}(r_{ij})b'_{ij}V_{\mathrm{A}}(r_{ij})\sum_{k\neq i,j}^{N}\delta_{i\beta}\delta_{j\alpha}f_{\mathrm{C}}(r_{ik})h(r_{ij}-r_{ik})g'(\cos\theta_{jik})\frac{r_{ik}^2-r_{jk}^2}{r_{ik}}\frac{1}{r_{ij}^2}\\&=-\frac{f_{\mathrm{C}}(r_{\beta\alpha})}{r_{\beta\alpha}^2}b'_{\beta\alpha}V_{\mathrm{A}}(r_{\beta\alpha})\sum_{k\neq\beta,\alpha}^{N}f_{\mathrm{C}}(r_{\beta k})h(r_{\beta\alpha}-r_{\beta k})g'(\cos\theta_{\alpha\beta k})\frac{r_{\beta k}^2-r_{\alpha k}^2}{r_{\beta k}}\\&=-\frac{f_{\mathrm{C}}(r_{\beta\alpha})}{r_{\beta\alpha}^2}b'_{\beta\alpha}V_{\mathrm{A}}(r_{\beta\alpha})\sum_{i\neq\beta,\alpha}^{N}f_{\mathrm{C}}(r_{\beta i})h(r_{\beta\alpha}-r_{\beta i})g'(\cos\theta_{\alpha\beta i})\frac{r_{\beta i}^2-r_{\alpha i}^2}{r_{\beta i}}\end{aligned}\tag{70}$$

$$\begin{aligned}C_{3,11}&=\sum_{i}^{N}\sum_{j\neq i}^{N}f_{\mathrm{C}}(r_{ij})b'_{ij}V_{\mathrm{A}}(r_{ij})\sum_{k\neq i,j}^{N}\delta_{i\alpha}\delta_{k\beta}f_{\mathrm{C}}(r_{ik})h(r_{ij}-r_{ik})g'(\cos\theta_{jik})\frac{\cos\theta_{jik}}{r_{ik}}\\&=\sum_{j\neq\alpha,\beta}^{N}f_{\mathrm{C}}(r_{\alpha j})b'_{\alpha j}V_{\mathrm{A}}(r_{\alpha j})f_{\mathrm{C}}(r_{\alpha\beta})h(r_{\alpha j}-r_{\alpha\beta})g'(\cos\theta_{j\alpha\beta})\frac{\cos\theta_{j\alpha\beta}}{r_{\alpha\beta}}\\&=\frac{f_{\mathrm{C}}(r_{\alpha\beta})}{r_{\alpha\beta}}\sum_{i\neq\alpha,\beta}^{N}f_{\mathrm{C}}(r_{\alpha i})b'_{\alpha i}V_{\mathrm{A}}(r_{\alpha i})h(r_{\alpha i}-r_{\alpha\beta})g'(\cos\theta_{i\alpha\beta})\cos\theta_{i\alpha\beta}\end{aligned}\tag{71}$$

$$\begin{aligned}
C_{3,12} &= -\sum_{i}^{N}\sum_{j\neq i}^{N} f_{\mathrm{C}}(r_{ij}) b'_{ij} V_{\mathrm{A}}(r_{ij}) \sum_{k\neq i,j}^{N} \delta_{i\alpha}\delta_{k\beta} f_{\mathrm{C}}(r_{ik}) h(r_{ij}-r_{ik}) g'(\cos\theta_{jik}) \frac{r_{ij}^2-r_{jk}^2}{r_{ij}} \frac{1}{r_{ik}^2} \\
&= -\sum_{j\neq\alpha,\beta}^{N} f_{\mathrm{C}}(r_{\alpha j}) b'_{\alpha j} V_{\mathrm{A}}(r_{\alpha j}) f_{\mathrm{C}}(r_{\alpha\beta}) h(r_{\alpha j}-r_{\alpha\beta}) g'(\cos\theta_{j\alpha\beta}) \frac{r_{\alpha j}^2-r_{j\beta}^2}{r_{\alpha j}} \frac{1}{r_{\alpha\beta}^2} \qquad (72) \\
&= -\frac{f_{\mathrm{C}}(r_{\alpha\beta})}{r_{\alpha\beta}^2} \sum_{i\neq\alpha,\beta}^{N} f_{\mathrm{C}}(r_{\alpha i}) b'_{\alpha i} V_{\mathrm{A}}(r_{\alpha i}) h(r_{\alpha i}-r_{\alpha\beta}) g'(\cos\theta_{i\alpha\beta}) \frac{r_{\alpha i}^2-r_{i\beta}^2}{r_{\alpha i}}
\end{aligned}$$

$$\begin{aligned}
C_{3,13} &= \sum_{i}^{N}\sum_{j\neq i}^{N} f_{\mathrm{C}}(r_{ij}) b'_{ij} V_{\mathrm{A}}(r_{ij}) \sum_{k\neq i,j}^{N} \delta_{i\beta}\delta_{k\alpha} f_{\mathrm{C}}(r_{ik}) h(r_{ij}-r_{ik}) g'(\cos\theta_{jik}) \frac{\cos\theta_{jik}}{r_{ik}} \\
&= \sum_{j\neq\beta,\alpha}^{N} f_{\mathrm{C}}(r_{\beta j}) b'_{\beta j} V_{\mathrm{A}}(r_{\beta j}) f_{\mathrm{C}}(r_{\beta\alpha}) h(r_{\beta j}-r_{\beta\alpha}) g'(\cos\theta_{j\beta\alpha}) \frac{\cos\theta_{j\beta\alpha}}{r_{\beta\alpha}} \qquad (73) \\
&= \frac{f_{\mathrm{C}}(r_{\beta\alpha})}{r_{\beta\alpha}} \sum_{i\neq\beta,\alpha}^{N} f_{\mathrm{C}}(r_{\beta i}) b'_{\beta i} V_{\mathrm{A}}(r_{\beta i}) h(r_{\beta i}-r_{\beta\alpha}) g'(\cos\theta_{i\beta\alpha}) \cos\theta_{i\beta\alpha}
\end{aligned}$$

$$\begin{aligned}
C_{3,14} &= -\sum_{i}^{N}\sum_{j\neq i}^{N} f_{\mathrm{C}}(r_{ij}) b'_{ij} V_{\mathrm{A}}(r_{ij}) \sum_{k\neq i,j}^{N} \delta_{i\beta}\delta_{k\alpha} f_{\mathrm{C}}(r_{ik}) h(r_{ij}-r_{ik}) g'(\cos\theta_{jik}) \frac{r_{ij}^2-r_{jk}^2}{r_{ij}} \frac{1}{r_{ik}^2} \\
&= -\sum_{j\neq\beta,\alpha}^{N} f_{\mathrm{C}}(r_{\beta j}) b'_{\beta j} V_{\mathrm{A}}(r_{\beta j}) f_{\mathrm{C}}(r_{\beta\alpha}) h(r_{\beta j}-r_{\beta\alpha}) g'(\cos\theta_{j\beta\alpha}) \frac{r_{\beta j}^2-r_{j\alpha}^2}{r_{\beta j}} \frac{1}{r_{\beta\alpha}^2} \qquad (74) \\
&= -\frac{f_{\mathrm{C}}(r_{\beta\alpha})}{r_{\beta\alpha}^2} \sum_{i\neq\beta,\alpha}^{N} f_{\mathrm{C}}(r_{\beta i}) b'_{\beta i} V_{\mathrm{A}}(r_{\beta i}) h(r_{\beta i}-r_{\beta\alpha}) g'(\cos\theta_{i\beta\alpha}) \frac{r_{\beta i}^2-r_{i\alpha}^2}{r_{\beta i}}
\end{aligned}$$

$$\begin{aligned}
C_{3,15} &= -\sum_{i}^{N}\sum_{j\neq i}^{N} f_{\mathrm{C}}(r_{ij}) b'_{ij} V_{\mathrm{A}}(r_{ij}) \sum_{k\neq i,j}^{N} \delta_{j\alpha}\delta_{k\beta} f_{\mathrm{C}}(r_{ik}) h(r_{ij}-r_{ik}) g'(\cos\theta_{jik}) \frac{r_{jk}}{r_{ij}r_{ik}} \\
&= -r_{\alpha\beta} \sum_{i\neq\alpha,\beta}^{N} \frac{f_{\mathrm{C}}(r_{i\alpha})}{r_{i\alpha}} b'_{i\alpha} V_{\mathrm{A}}(r_{i\alpha}) \frac{f_{\mathrm{C}}(r_{i\beta})}{r_{i\beta}} h(r_{i\alpha}-r_{i\beta}) g'(\cos\theta_{\alpha i\beta}) \qquad (75)
\end{aligned}$$

and

$$\begin{aligned}
C_{3,16} &= -\sum_{i}^{N}\sum_{j\neq i}^{N} f_{\mathrm{C}}(r_{ij}) b'_{ij} V_{\mathrm{A}}(r_{ij}) \sum_{k\neq i,j}^{N} \delta_{j\beta}\delta_{k\alpha} f_{\mathrm{C}}(r_{ik}) h(r_{ij}-r_{ik}) g'(\cos\theta_{jik}) \frac{r_{jk}}{r_{ij}r_{ik}} \\
&= -r_{\beta\alpha} \sum_{i\neq\beta,\alpha}^{N} \frac{f_{\mathrm{C}}(r_{i\beta})}{r_{i\beta}} b'_{i\beta} V_{\mathrm{A}}(r_{i\beta}) \frac{f_{\mathrm{C}}(r_{i\alpha})}{r_{i\alpha}} h(r_{i\beta}-r_{i\alpha}) g'(\cos\theta_{\beta i\alpha}) \qquad (76)
\end{aligned}$$

At this point it is worth analyzing the structure of A_3. It is composed of two equivalent sets of eight terms, which transform into each other under the following exchange of indices:

$$(\alpha,\beta,i) \leftrightarrow (\beta,\alpha,i) \qquad (77)$$

This can be written as:

$$A_3 = \frac{1}{2}\left[A_{3,\alpha\beta} + A_{3,\beta\alpha}\right] \qquad (78)$$

where

$$A_{3,\alpha\beta} = C_{3,1} + C_{3,3} + C_{3,5} + C_{3,7} + C_{3,8} + C_{3,11} + C_{3,12} + C_{3,15} \tag{79}$$

$$A_{3,\beta\alpha} = C_{3,2} + C_{3,4} + C_{3,6} + C_{3,9} + C_{3,10} + C_{3,13} + C_{3,14} + C_{3,16} \tag{80}$$

In what follows we will focus only on the first term $A_{3,\alpha\beta}$.

It can be further simplified by a pairwise combining of its terms. By adding $C_{3,7}$ and $C_{3,8}$ we get:

$$\begin{aligned}
C_{3,7} + C_{3,8} = {} & \frac{f_{\mathrm{C}}(r_{\alpha\beta})}{r_{\alpha\beta}} b'_{\alpha\beta} V_{\mathrm{A}}(r_{\alpha\beta}) \sum_{i\neq\alpha,\beta}^{N} f_{\mathrm{C}}(r_{\alpha i}) h(r_{\alpha\beta} - r_{\alpha i}) g'(\cos\theta_{\beta\alpha i}) \cos\theta_{\beta\alpha i} - \\
& \frac{f_{\mathrm{C}}(r_{\alpha\beta})}{r_{\alpha\beta}^2} b'_{\alpha\beta} V_{\mathrm{A}}(r_{\alpha\beta}) \sum_{i\neq\alpha,\beta}^{N} f_{\mathrm{C}}(r_{\alpha i}) h(r_{\alpha\beta} - r_{\alpha i}) g'(\cos\theta_{\beta\alpha i}) \frac{r_{\alpha i}^2 - r_{\beta i}^2}{r_{\alpha i}} \\
= {} & \frac{f_{\mathrm{C}}(r_{\alpha\beta})}{r_{\alpha\beta}^2} b'_{\alpha\beta} V_{\mathrm{A}}(r_{\alpha\beta}) \sum_{i\neq\alpha,\beta}^{N} f_{\mathrm{C}}(r_{\alpha i}) h(r_{\alpha\beta} - r_{\alpha i}) g'(\cos\theta_{\beta\alpha i}) \times \\
& \left[r_{\alpha\beta} \cos\theta_{\beta\alpha i} - \frac{r_{\alpha i}^2 - r_{\beta i}^2}{r_{\alpha i}} \right]
\end{aligned} \tag{81}$$

The cosine rule (4) allows us to write:

$$\frac{r_{\alpha i}^2 - r_{\beta i}^2}{r_{\alpha i}} = 2 r_{\alpha\beta} \cos\theta_{\beta\alpha i} - \frac{r_{\alpha\beta}^2}{r_{\alpha i}} \tag{82}$$

which can be used to simplify Equation (81):

$$\begin{aligned}
C_{3,7} + C_{3,8} = {} & \frac{f_{\mathrm{C}}(r_{\alpha\beta})}{r_{\alpha\beta}^2} b'_{\alpha\beta} V_{\mathrm{A}}(r_{\alpha\beta}) \sum_{i\neq\alpha,\beta}^{N} f_{\mathrm{C}}(r_{\alpha i}) h(r_{\alpha\beta} - r_{\alpha i}) g'(\cos\theta_{\beta\alpha i}) \times \\
& \left[r_{\alpha\beta} \cos\theta_{\beta\alpha i} - \frac{r_{\alpha i}^2 - r_{\beta i}^2}{r_{\alpha i}} \right] \\
= {} & \frac{f_{\mathrm{C}}(r_{\alpha\beta})}{r_{\alpha\beta}^2} b'_{\alpha\beta} V_{\mathrm{A}}(r_{\alpha\beta}) \sum_{i\neq\alpha,\beta}^{N} f_{\mathrm{C}}(r_{\alpha i}) h(r_{\alpha\beta} - r_{\alpha i}) g'(\cos\theta_{\beta\alpha i}) \times \\
& \left[r_{\alpha\beta} \cos\theta_{\beta\alpha i} - 2 r_{\alpha\beta} \cos\theta_{\beta\alpha i} + \frac{r_{\alpha\beta}^2}{r_{\alpha i}} \right] \\
= {} & \frac{f_{\mathrm{C}}(r_{\alpha\beta})}{r_{\alpha\beta}^2} b'_{\alpha\beta} V_{\mathrm{A}}(r_{\alpha\beta}) \sum_{i\neq\alpha,\beta}^{N} f_{\mathrm{C}}(r_{\alpha i}) h(r_{\alpha\beta} - r_{\alpha i}) g'(\cos\theta_{\beta\alpha i}) \times \\
& \left[- r_{\alpha\beta} \cos\theta_{\beta\alpha i} + \frac{r_{\alpha\beta}^2}{r_{\alpha i}} \right] \\
= {} & - \frac{f_{\mathrm{C}}(r_{\alpha\beta})}{r_{\alpha\beta}} b'_{\alpha\beta} V_{\mathrm{A}}(r_{\alpha\beta}) \sum_{i\neq\alpha,\beta}^{N} f_{\mathrm{C}}(r_{\alpha i}) h(r_{\alpha\beta} - r_{\alpha i}) g'(\cos\theta_{\beta\alpha i}) \cos\theta_{\beta\alpha i} + \\
& f_{\mathrm{C}}(r_{\alpha\beta}) b'_{\alpha\beta} V_{\mathrm{A}}(r_{\alpha\beta}) \sum_{i\neq\alpha,\beta}^{N} \frac{f_{\mathrm{C}}(r_{\alpha i})}{r_{\alpha i}} h(r_{\alpha\beta} - r_{\alpha i}) g'(\cos\theta_{\beta\alpha i})
\end{aligned} \tag{83}$$

In a similar way we can elaborate the sum of $C_{3,11}$ and $C_{3,12}$, which will be given as:

$$\begin{aligned}
C_{3,11}+C_{3,12} &= \frac{f_{\mathrm{C}}(r_{\alpha\beta})}{r_{\alpha\beta}} \sum_{i\neq\alpha,\beta}^{N} f_{\mathrm{C}}(r_{\alpha i}) b'_{\alpha i} V_{\mathrm{A}}(r_{\alpha i}) h(r_{\alpha i}-r_{\alpha\beta}) g'(\cos\theta_{i\alpha\beta}) \cos\theta_{i\alpha\beta} - \\
&\quad \frac{f_{\mathrm{C}}(r_{\alpha\beta})}{r_{\alpha\beta}^2} \sum_{i\neq\alpha,\beta}^{N} f_{\mathrm{C}}(r_{\alpha i}) b'_{\alpha i} V_{\mathrm{A}}(r_{\alpha i}) h(r_{\alpha i}-r_{\alpha\beta}) g'(\cos\theta_{i\alpha\beta}) \frac{r_{\alpha i}^2 - r_{i\beta}^2}{r_{\alpha i}} \\
&= \frac{f_{\mathrm{C}}(r_{\alpha\beta})}{r_{\alpha\beta}^2} \sum_{i\neq\alpha,\beta}^{N} f_{\mathrm{C}}(r_{\alpha i}) b'_{\alpha i} V_{\mathrm{A}}(r_{\alpha i}) h(r_{\alpha i}-r_{\alpha\beta}) g'(\cos\theta_{i\alpha\beta}) \times \\
&\quad \left[r_{\alpha\beta} \cos\theta_{i\alpha\beta} - \frac{r_{\alpha i}^2 - r_{i\beta}^2}{r_{\alpha i}} \right] \\
&= \frac{f_{\mathrm{C}}(r_{\alpha\beta})}{r_{\alpha\beta}^2} \sum_{i\neq\alpha,\beta}^{N} f_{\mathrm{C}}(r_{\alpha i}) b'_{\alpha i} V_{\mathrm{A}}(r_{\alpha i}) h(r_{\alpha i}-r_{\alpha\beta}) g'(\cos\theta_{i\alpha\beta}) \times \\
&\quad \left[r_{\alpha\beta} \cos\theta_{i\alpha\beta} - 2 r_{\alpha\beta} \cos\theta_{i\alpha\beta} + \frac{r_{\alpha\beta}^2}{r_{\alpha i}} \right] \\
&= \frac{f_{\mathrm{C}}(r_{\alpha\beta})}{r_{\alpha\beta}^2} \sum_{i\neq\alpha,\beta}^{N} f_{\mathrm{C}}(r_{\alpha i}) b'_{\alpha i} V_{\mathrm{A}}(r_{\alpha i}) h(r_{\alpha i}-r_{\alpha\beta}) g'(\cos\theta_{i\alpha\beta}) \times \\
&\quad \left[- r_{\alpha\beta} \cos\theta_{i\alpha\beta} + \frac{r_{\alpha\beta}^2}{r_{\alpha i}} \right] \\
&= -\frac{f_{\mathrm{C}}(r_{\alpha\beta})}{r_{\alpha\beta}} \sum_{i\neq\alpha,\beta}^{N} f_{\mathrm{C}}(r_{\alpha i}) b'_{\alpha i} V_{\mathrm{A}}(r_{\alpha i}) h(r_{\alpha i}-r_{\alpha\beta}) g'(\cos\theta_{i\alpha\beta}) \cos\theta_{i\alpha\beta} + \\
&\quad f_{\mathrm{C}}(r_{\alpha\beta}) \sum_{i\neq\alpha,\beta}^{N} \frac{f_{\mathrm{C}}(r_{\alpha i})}{r_{\alpha i}} b'_{\alpha i} V_{\mathrm{A}}(r_{\alpha i}) h(r_{\alpha i}-r_{\alpha\beta}) g'(\cos\theta_{i\alpha\beta})
\end{aligned} \tag{84}$$

This almost completes the simplification of $A_{3,\alpha\beta}$, which, owing to (61), (63), (65), (83), (84) and (75), can be written as:

$$\begin{aligned}
A_{3,\alpha\beta} &= C_{3,1} + C_{3,3} + C_{3,5} + \left(C_{3,7} + C_{3,8}\right) + \left(C_{3,11} + C_{3,12}\right) + C_{3,15} \\
&= f'_{\mathrm{C}}(r_{\alpha\beta}) \sum_{i\neq\alpha,\beta}^{N} f_{\mathrm{C}}(r_{\alpha i}) b'_{\alpha i} V_{\mathrm{A}}(r_{\alpha i}) h(r_{\alpha i}-r_{\alpha\beta}) g(\cos\theta_{i\alpha\beta}) + \\
&\quad f_{\mathrm{C}}(r_{\alpha\beta}) b'_{\alpha\beta} V_{\mathrm{A}}(r_{\alpha\beta}) \sum_{i\neq\alpha,\beta}^{N} f_{\mathrm{C}}(r_{\alpha i}) h'(r_{\alpha\beta}-r_{\alpha i}) g(\cos\theta_{\beta\alpha i}) - \\
&\quad f_{\mathrm{C}}(r_{\alpha\beta}) \sum_{i\neq\alpha,\beta}^{N} f_{\mathrm{C}}(r_{\alpha i}) b'_{\alpha i} V_{\mathrm{A}}(r_{\alpha i}) h'(r_{\alpha i}-r_{\alpha\beta}) g(\cos\theta_{i\alpha\beta}) - \\
&\quad \frac{f_{\mathrm{C}}(r_{\alpha\beta})}{r_{\alpha\beta}} b'_{\alpha\beta} V_{\mathrm{A}}(r_{\alpha\beta}) \sum_{i\neq\alpha,\beta}^{N} f_{\mathrm{C}}(r_{\alpha i}) h(r_{\alpha\beta}-r_{\alpha i}) g'(\cos\theta_{\beta\alpha i}) \cos\theta_{\beta\alpha i} + \qquad (85) \\
&\quad f_{\mathrm{C}}(r_{\alpha\beta}) b'_{\alpha\beta} V_{\mathrm{A}}(r_{\alpha\beta}) \sum_{i\neq\alpha,\beta}^{N} \frac{f_{\mathrm{C}}(r_{\alpha i})}{r_{\alpha i}} h(r_{\alpha\beta}-r_{\alpha i}) g'(\cos\theta_{\beta\alpha i}) -
\end{aligned}$$

$$\frac{f_{\mathrm{C}}(r_{\alpha\beta})}{r_{\alpha\beta}}\sum_{i\neq\alpha,\beta}^{N} f_{\mathrm{C}}(r_{\alpha i})b'_{\alpha i}V_{\mathrm{A}}(r_{\alpha i})h(r_{\alpha i}-r_{\alpha\beta})g'(\cos\theta_{i\alpha\beta})\cos\theta_{i\alpha\beta}+$$

$$f_{\mathrm{C}}(r_{\alpha\beta})\sum_{i\neq\alpha,\beta}^{N}\frac{f_{\mathrm{C}}(r_{\alpha i})}{r_{\alpha i}}b'_{\alpha i}V_{\mathrm{A}}(r_{\alpha i})h(r_{\alpha i}-r_{\alpha\beta})g'(\cos\theta_{i\alpha\beta})-$$

$$r_{\alpha\beta}\sum_{i\neq\alpha,\beta}^{N}\frac{f_{\mathrm{C}}(r_{i\alpha})}{r_{i\alpha}}b'_{i\alpha}V_{\mathrm{A}}(r_{i\alpha})\frac{f_{\mathrm{C}}(r_{i\beta})}{r_{i\beta}}h(r_{i\alpha}-r_{i\beta})g'(\cos\theta_{\alpha i\beta})$$

This can be written in a more compact way as:

$$\begin{aligned}
A_{3,\alpha\beta}=\;&f'_{\mathrm{C}}(r_{\alpha\beta})\sum_{i\neq\alpha,\beta}^{N} f_{\mathrm{C}}(r_{\alpha i})b'_{\alpha i}V_{\mathrm{A}}(r_{\alpha i})h(r_{\alpha i}-r_{\alpha\beta})g(\cos\theta_{i\alpha\beta})+\\
&f_{\mathrm{C}}(r_{\alpha\beta})b'_{\alpha\beta}V_{\mathrm{A}}(r_{\alpha\beta})\times\left[\sum_{i\neq\alpha,\beta}^{N} f_{\mathrm{C}}(r_{\alpha i})h'(r_{\alpha\beta}-r_{\alpha i})g(\cos\theta_{\beta\alpha i})-\right.\\
&\left.\sum_{i\neq\alpha,\beta}^{N}\left(\frac{1}{r_{\alpha\beta}}\cos\theta_{\beta\alpha i}-\frac{1}{r_{\alpha i}}\right)f_{\mathrm{C}}(r_{\alpha i})h(r_{\alpha\beta}-r_{\alpha i})g'(\cos\theta_{\beta\alpha i})\right]-\\
&f_{\mathrm{C}}(r_{\alpha\beta})\sum_{i\neq\alpha,\beta}^{N} f_{\mathrm{C}}(r_{\alpha i})b'_{\alpha i}V_{\mathrm{A}}(r_{\alpha i})\times\\
&\left[h'(r_{\alpha i}-r_{\alpha\beta})g(\cos\theta_{i\alpha\beta})+\left(\frac{1}{r_{\alpha\beta}}\cos\theta_{i\alpha\beta}-\frac{1}{r_{\alpha i}}\right)h(r_{\alpha i}-r_{\alpha\beta})g'(\cos\theta_{i\alpha\beta})\right]-\\
&r_{\alpha\beta}\sum_{i\neq\alpha,\beta}^{N}\frac{f_{\mathrm{C}}(r_{i\alpha})}{r_{i\alpha}}\frac{f_{\mathrm{C}}(r_{i\beta})}{r_{i\beta}}b'_{i\alpha}V_{\mathrm{A}}(r_{i\alpha})h(r_{i\alpha}-r_{i\beta})g'(\cos\theta_{\alpha i\beta})
\end{aligned}\tag{86}$$

This completes the elaboration of the $A_{3,\alpha\beta}$ term. We remind that the $A_{3,\beta\alpha}$ term is obtained from $A_{3,\alpha\beta}$ by exchanging α and β indices.

Now, since we have found the expression for $\partial E_{\mathrm{tot}}/\partial r_{\alpha\beta}$, we are ready to give the expression for the central force $\mathbf{F}_{\alpha\beta}$. Returning to the original indices i, j and k, and employing intermediate results of (22), (26), (28), (78) and (86), we can express the central force with which particle j acts on particle i as:

$$\begin{aligned}
\mathbf{F}_{ij}=\frac{\mathbf{r}_{ij}}{r_{ij}}\times\Bigg\{&f'_{\mathrm{C}}(r_{ij})\left[V_{\mathrm{R}}(r_{ij})+\frac{b_{ij}+b_{ji}}{2}V_{\mathrm{A}}(r_{ij})\right]+f_{\mathrm{C}}(r_{ij})\left[V'_{\mathrm{R}}(r_{ij})+\frac{b_{ij}+b_{ji}}{2}V'_{\mathrm{A}}(r_{ij})\right]+\\
&\frac{1}{2}f'_{\mathrm{C}}(r_{ij})\sum_{k\neq i,j}^{N} f_{\mathrm{C}}(r_{ik})b'_{ik}V_{\mathrm{A}}(r_{ik})h(r_{ik}-r_{ij})g(\cos\theta_{jik})+\\
&\frac{1}{2}f_{\mathrm{C}}(r_{ij})b'_{ij}V_{\mathrm{A}}(r_{ij})\times\left[\sum_{k\neq i,j}^{N} f_{\mathrm{C}}(r_{ik})h'(r_{ij}-r_{ik})g(\cos\theta_{jik})-\right.\\
&\left.\sum_{k\neq i,j}^{N}\left(\frac{1}{r_{ij}}\cos\theta_{jik}-\frac{1}{r_{ik}}\right)f_{\mathrm{C}}(r_{ik})h(r_{ij}-r_{ik})g'(\cos\theta_{jik})\right]-\\
&\frac{1}{2}f_{\mathrm{C}}(r_{ij})\sum_{k\neq i,j}^{N} f_{\mathrm{C}}(r_{ik})b'_{ik}V_{\mathrm{A}}(r_{ik})\times
\end{aligned}$$

$$
\begin{aligned}
&\left[h'(r_{ik}-r_{ij})g(\cos\theta_{jik})+\left(\frac{1}{r_{ij}}\cos\theta_{jik}-\frac{1}{r_{ik}}\right)h(r_{ik}-r_{ij})g'(\cos\theta_{jik})\right]+\\
&\frac{1}{2}f'_{\mathrm{C}}(r_{ji})\sum_{k\neq j,i}^{N}f_{\mathrm{C}}(r_{jk})b'_{jk}V_{\mathrm{A}}(r_{jk})h(r_{jk}-r_{ji})g(\cos\theta_{ijk})+ \qquad (87)\\
&\frac{1}{2}f_{\mathrm{C}}(r_{ji})b'_{ji}V_{\mathrm{A}}(r_{ji})\times\left[\sum_{k\neq j,i}^{N}f_{\mathrm{C}}(r_{jk})h'(r_{ji}-r_{jk})g(\cos\theta_{ijk})-\right.\\
&\left.\sum_{k\neq j,i}^{N}\left(\frac{1}{r_{ji}}\cos\theta_{ijk}-\frac{1}{r_{jk}}\right)f_{\mathrm{C}}(r_{jk})h(r_{ji}-r_{jk})g'(\cos\theta_{ijk})\right]-\\
&\frac{1}{2}f_{\mathrm{C}}(r_{ji})\sum_{k\neq j,i}^{N}f_{\mathrm{C}}(r_{jk})b'_{jk}V_{\mathrm{A}}(r_{jk})\times\\
&\left[h'(r_{jk}-r_{ji})g(\cos\theta_{ijk})+\left(\frac{1}{r_{ji}}\cos\theta_{ijk}-\frac{1}{r_{jk}}\right)h(r_{jk}-r_{ji})g'(\cos\theta_{ijk})\right]-\\
&\frac{1}{2}r_{ij}\sum_{k\neq i,j}^{N}\frac{f_{\mathrm{C}}(r_{ki})}{r_{ki}}\frac{f_{\mathrm{C}}(r_{kj})}{r_{kj}}g'(\cos\theta_{ikj})\times\\
&\left.\left[b'_{ki}V_{\mathrm{A}}(r_{ki})h(r_{ki}-r_{kj})+b'_{kj}V_{\mathrm{A}}(r_{kj})h(r_{kj}-r_{ki})\right]\right\}
\end{aligned}
$$

The derivatives $f'_{\mathrm{C}}(r)$, $V'_{\mathrm{R}}(r)$, $V'_{\mathrm{A}}(r)$, b'_{ij}, $h'(r)$, and $g'(\cos\theta)$ are given by Equations (29), (30), (31), (33), (37) and (38), respectively. When writing the final expression we used the fact that $\cos\theta_{jik}=\cos\theta_{kij}$. We also combined the last terms of $A_{3,\alpha\beta}$ and $A_{3,\beta\alpha}$ and wrote them together.

4. Discussion

Before we will discuss the properties of the obtained central-force decomposition (87) it is worth introducing some short notation which will facilitate further analysis. Therefore, for the sake of brevity, we will denote the sums appearing in (87) as follows:

1. $\Theta^{(1)}_{jik}$, $\Theta^{(2)}_{jik}$, $\Theta^{(3)}_{jik}$, $\Theta^{(4)}_{jik}$ – sums containing $\cos\theta_{jik}$,
2. $\Theta^{(1)}_{ijk}$, $\Theta^{(2)}_{ijk}$, $\Theta^{(3)}_{ijk}$, $\Theta^{(4)}_{ijk}$ – sums containing $\cos\theta_{ijk}$,
3. $\Theta^{(5)}_{ikj}$ – sum containing $\cos\theta_{ikj}$.

Using this notation we can rewrite Equation (87) as:

$$
\begin{aligned}
\mathbf{F}_{ij}=\frac{\mathbf{r}_{ij}}{r_{ij}}\times\Bigg\{&f'_{\mathrm{C}}(r_{ij})\left[V_{\mathrm{R}}(r_{ij})+\frac{b_{ij}+b_{ji}}{2}V_{\mathrm{A}}(r_{ij})\right]+f_{\mathrm{C}}(r_{ij})\left[V'_{\mathrm{R}}(r_{ij})+\frac{b_{ij}+b_{ji}}{2}V'_{\mathrm{A}}(r_{ij})\right]+\\
&\frac{1}{2}f'_{\mathrm{C}}(r_{ij})\Theta^{(1)}_{jik}+\frac{1}{2}f_{\mathrm{C}}(r_{ij})b'_{ij}V_{\mathrm{A}}(r_{ij})\times\left[\Theta^{(2)}_{jik}-\Theta^{(3)}_{jik}\right]-\frac{1}{2}f_{\mathrm{C}}(r_{ij})\Theta^{(4)}_{jik}+ \qquad (88)
\end{aligned}
$$

$$\frac{1}{2}f'_{\mathrm{C}}(r_{ji})\Theta^{(1)}_{ijk}+\frac{1}{2}f_{\mathrm{C}}(r_{ji})b'_{ji}V_{\mathrm{A}}(r_{ji})\times\left[\Theta^{(2)}_{ijk}-\Theta^{(3)}_{ijk}\right]-\frac{1}{2}f_{\mathrm{C}}(r_{ji})\Theta^{(4)}_{ijk}-$$

$$\left.\frac{1}{2}r_{ij}\Theta^{(5)}_{ikj}\right\}$$

where

$$\Theta^{(1)}_{jik}=\sum_{k\neq i,j}^{N}f_{\mathrm{C}}(r_{ik})b'_{ik}V_{\mathrm{A}}(r_{ik})h(r_{ik}-r_{ij})g(\cos\theta_{jik}) \tag{89}$$

$$\Theta^{(2)}_{jik}=\sum_{k\neq i,j}^{N}f_{\mathrm{C}}(r_{ik})h'(r_{ij}-r_{ik})g(\cos\theta_{jik}) \tag{90}$$

$$\Theta^{(3)}_{jik}=\sum_{k\neq i,j}^{N}\left(\frac{1}{r_{ij}}\cos\theta_{jik}-\frac{1}{r_{ik}}\right)f_{\mathrm{C}}(r_{ik})h(r_{ij}-r_{ik})g'(\cos\theta_{jik}) \tag{91}$$

$$\Theta^{(4)}_{jik}=\sum_{k\neq i,j}^{N}f_{\mathrm{C}}(r_{ik})b'_{ik}V_{\mathrm{A}}(r_{ik})\times \tag{92}$$
$$\left[h'(r_{ik}-r_{ij})g(\cos\theta_{jik})+\left(\frac{1}{r_{ij}}\cos\theta_{jik}-\frac{1}{r_{ik}}\right)h(r_{ik}-r_{ij})g'(\cos\theta_{jik})\right]$$

and

$$\Theta^{(5)}_{ikj}=\sum_{k\neq i,j}^{N}\frac{f_{\mathrm{C}}(r_{ki})}{r_{ki}}\frac{f_{\mathrm{C}}(r_{kj})}{r_{kj}}g'(\cos\theta_{ikj})\times \tag{93}$$
$$\left[b'_{ki}V_{\mathrm{A}}(r_{ki})h(r_{ki}-r_{kj})+b'_{kj}V_{\mathrm{A}}(r_{kj})h(r_{kj}-r_{ki})\right]$$

The $\Theta^{(1)}_{ijk}-\Theta^{(4)}_{ijk}$ sums are obtained from Equations (89)–(92) by exchanging indices i and j.

In what follows we will identify atoms which contribute to the central force $\mathbf{F}_{ij}$ with which atom j acts on atom i. It is even intuitive that this force depends mostly on the positions of atoms i and j. This is evidenced by the fact that all the terms of Equation (87) depend on $\mathbf{r}_i$ or $\mathbf{r}_j$, being functions of r_{ij}, r_{ik} and r_{jk}. The central force $\mathbf{F}_{ij}$ depends also on the positions of other atoms, which is a consequence of the many-body character of the Tersoff potential. In what follows we will analyse which other atoms $k\neq i,j$ contribute to $\mathbf{F}_{ij}$. We will answer this question by analysing the structure of Equation (88), with particular focus on the $\Theta^{(1)}_{jik}-\Theta^{(4)}_{jik}$, $\Theta^{(1)}_{ijk}-\Theta^{(4)}_{ijk}$ and $\Theta^{(5)}_{ikj}$ sums.

All the terms of Equation (88) contain the cutoff function $f_{\mathrm{C}}(r)$ and/or its derivative $f'_{\mathrm{C}}(r)$, both of which are zero above the cutoff radius r_{c}, which for the Tersoff potential is equal to $r_{\mathrm{c}}=R+D$ (compare with Equation (9)). The presence of these functions is the reason why the first eight sums of Equation (88):

(i) either run over the nearest neighbours of atom i (this holds for sums $\Theta^{(1)}_{jik}-\Theta^{(4)}_{jik}$ and is evidenced by the fact, that $f_{\mathrm{C}}(r_{ik})$ – which is nonzero only for atoms k which are the nearest neighbours of atom i – appears in these sums, as an element of the product),

(ii) or run over the nearest neighbours of atom j (this holds for sums $\Theta^{(1)}_{ijk}-\Theta^{(4)}_{ijk}$ and can be explained by the presence of $f_{\mathrm{C}}(r_{jk})$).

Therefore it is concluded that the corresponding terms of Equation (88) describe:

(i) the influence of the nearest neighbourhood of atom i on the central force $\mathbf{F}_{ij}$ (second line of Equation (88), *i.e.* terms from 3rd to 5th),

(ii) the influence of the nearest neighbourhood of atom j on the central force $\mathbf{F}_{ij}$ (third line of Equation (88), *i.e.* terms from 6th to 8th).

It is worth noting that these contributions are nonzero only if the central force between atoms which are nearest neighbours is considered. This originates from the fact that:

(i) $f'_{\mathrm{C}}(r_{ij})$ and $f_{\mathrm{C}}(r_{ij})$ appear before sums $\Theta^{(1)}_{jik}-\Theta^{(4)}_{jik}$ (second line of Equation (88)),

(ii) $f'_{\mathrm{C}}(r_{ji})$ and $f_{\mathrm{C}}(r_{ji})$ appear before sums $\Theta^{(1)}_{ijk}-\Theta^{(4)}_{ijk}$ (third line of Equation (88)).

The above observations are also true for the first two terms of $\mathbf{F}_{ij}$ (fist line of Equation (88)), which also encopass the nearest neighbours of atoms i and j, because of the presence of the bond orders b_{ij} and b_{ji}. However, the repulsive part, *i.e.*

$$f'_{\mathrm{C}}(r_{ij})V_{\mathrm{R}}(r_{ij})+f_{\mathrm{C}}(r_{ij})V'_{\mathrm{R}}(r_{ij}) \tag{94}$$

must be excluded from this generalization as it describes – in fact, the only – purely two body contributions to the central force $\mathbf{F}_{ij}$.

The analysis of the last term of Equation (88), *i.e.*

$$-\frac{1}{2}r_{ij}\Theta^{(5)}_{ikj} \tag{95}$$

reveals its somewhat different role. First of all, this term does not vanish for atoms i and j which are *not* nearest neighbours, which is evidenced by the fact that none of the $f_{\mathrm{C}}(r_{ij})$, $f'_{\mathrm{C}}(r_{ij})$, $f_{\mathrm{C}}(r_{ji})$, $f'_{\mathrm{C}}(r_{ji})$ functions appears in its definition. A further analysis of this term shows that it describes the contributions to $\mathbf{F}_{ij}$ which depend on the positions of atoms which are common neighbours of atoms i and j. This originates from the fact that the $\Theta^{(5)}_{ikj}$ sum runs over the atoms which – at the same time – belong to the nearest neighbours of atom i and atom j, as indicated by the presence of the product $f_{\mathrm{C}}(r_{ki})f_{\mathrm{C}}(r_{kj})$ in Equation (93).

The significant dissimilarity of the last term becomes better visible when one tries to identify pairs of atoms for which the central force $\mathbf{F}_{ij}$ is non-vanishing. In this case the analysis of the last term leads to the conclusion that two atoms i and j may interact centrally even if they are *not* nearest neighbours. For such atoms the central force $\mathbf{F}_{ij}$ may be non-zero if (and only if) there is at least one atom k which is – at the same time – the nearest neighbour of atom i (providing

$f_\mathrm{C}(r_{ki}) \neq 0$) and the nearest neighbour of atom j (providing $f_\mathrm{C}(r_{kj}) \neq 0$). This means that two atoms i and j that are separated by $r_\mathrm{c} \leq r_{ij} < 2r_\mathrm{c}$ may interact centrally. For such pairs (characterized by $f_\mathrm{C}(r_{ij}) = f'_\mathrm{C}(r_{ij}) = 0$) the central force is completely given by the last term of Equation (87), *i.e.*:

$$\begin{aligned}\mathbf{F}_{ij} = \frac{\mathbf{r}_{ij}}{r_{ij}}\left(-\frac{1}{2}r_{ij}\Theta^{(5)}_{ikj}\right) = -\frac{1}{2}\mathbf{r}_{ij}\sum_{k\neq i,j}^{N}\frac{f_\mathrm{C}(r_{ki})}{r_{ki}}\frac{f_\mathrm{C}(r_{kj})}{r_{kj}}g'(\cos\theta_{ikj})\times \\ \left[b'_{ki}V_\mathrm{A}(r_{ki})h(r_{ki}-r_{kj}) + b'_{kj}V_\mathrm{A}(r_{kj})h(r_{kj}-r_{ki})\right]\end{aligned} \tag{96}$$

To complete the picture it is worth noting that the central force $\mathbf{F}_{ij}$ vanishes identically, *i.e.* $\mathbf{F}_{ij} \equiv \mathbf{0}$, when the distance between atoms i and j is greater or equal $2r_\mathrm{c}$.

The above observations lead to another important conclusion. Despite the fact that it explicitly includes a cutoff radius r_c, the Tersoff potential has an effective cutoff radius (in the sense of non-vanishing central forces) of $2r_\mathrm{c}$. This conclusion shows the similarity of the Tersoff potential to the spline based modified embedded atom method potential, for which the same conclusion was drawn in [33], also based on the analysis of the obtained CFD.

5. Summary

In this work we derived a central-force decomposition for the Tersoff potential, which is commonly used in atomistic simulations to describe interatomic interactions in covalently bonded materials. The main outcome of this work is the expression (87). We followed the derivation with a brief discussion of the obtained decomposition, demonstrating that the Tersoff potential is characterised by non-vanishing central interactions between not only first-nearest, but also second-nearest neighbours.

In this work we did not present any application of the obtained decomposition. However, we note that there are many computational techniques which require the CFD as a prerequisite. For an overview of the methods which benefit from the CFD we refer the interested Reader to our previous work [33] where we have presented the CFD of the spline-based modified embedded atom method potential and applied it to study stress fields around edge dislocation in bcc molybdenum. We hope that in the near future we will be able to present the results of similar (*i.e.* also employing Hardy's formalism) studies on the stress fields around point defects in carbon nanostructures modeled with the Tersoff potential.

References

[1] Alder B J and Wainwright T E 1959 *The Journal of Chemical Physics* **31** 459
[2] Rapaport D C 1995 *The Art of Molecular Dynamics Simulation*, Cambridge University Press
[3] Leach A R 2001 *Molecular Modelling: Principles and Applications*, Prentice Hall
[4] Frenkel D and Smit B 2002 *Understanding Molecular Simulations: From Algorithms to Applications*, Academic Press

[5] Voter A F 1996 *MRS Bulletin*, Cambridge University Press, **21** (2) 17 doi: 10.1557/S0883769400046248

[6] Dziedzic J, Winczewski S and Rybicki J 2016 *Computational Materials Science* **114** (Supplement C) 219 doi: 10.1016/j.commatsci.2015.12.014

[7] Stillinger F H and Weber T A 1985 *Phys. Rev. B*, American Physical Society, **31** (8) 5262 doi: 10.1103/PhysRevB.31.5262

[8] Daw M S and Baskes M I 1984 *Phys. Rev. B*, American Physical Society, **29** (12) 6443 doi: 10.1103/PhysRevB.29.6443

[9] Baskes M I 1987 *Phys. Rev. Lett.*, American Physical Society, **59** (23) 2666 doi: 10.1103/PhysRevLett.59.2666

[10] Baskes M I 1992 *Phys. Rev. B*, American Physical Society, **46** (5) 2727 doi: 10.1103/PhysRevB.46.2727

[11] Lee B-J and Baskes M I 2000 *Phys. Rev. B*, American Physical Society, **62** (13) 8564 doi: 10.1103/PhysRevB.62.8564

[12] Dongare A M, Neurock M and Zhigilei L V 2009 *Phys. Rev. B*, American Physical Society, **80** (18) 184106 doi: 10.1103/PhysRevB.80.184106

[13] Lenosky T J, Sadigh B, Alonso E, Bulatov V V, Rubia T D de la, Kim J, Voter A F and Kress J D 2000 *Modelling and Simulation in Materials Science and Engineering* **8** (6) 825

[14] Brenner D W 1990 *Phys. Rev. B*, American Physical Society, **42** (15) 9458 doi: 10.1103/PhysRevB.42.9458

[15] Stuart S J, Tutein A B and Harrison J A 2000 *The Journal of Chemical Physics* **112** (14) 6472 doi: 10.1063/1.481208

[16] Brenner D W, Shenderova O A, Harrison J A, Stuart S J, Ni B and Sinnott S B 2002 *Journal of Physics: Condensed Matter* **14** (4) 783

[17] Tersoff J 1988 *Phys. Rev. B*, American Physical Society, **37** (12) 6991 doi: 10.1103/PhysRevB.37.6991

[18] Tersoff J 1989 *Phys. Rev. B*, American Physical Society, **39** (8) 5566 doi: 10.1103/PhysRevB.39.5566

[19] Erhart P and Albe K 2005 *Phys. Rev. B*, American Physical Society, **71** (3) 35211 doi: 10.1103/PhysRevB.71.035211

[20] Lindsay L and Broido D A 2010 *Phys. Rev. B*, American Physical Society, **81** (20) 205441 doi: 10.1103/PhysRevB.81.205441

[21] Agrawal P M, Raff L M and Komanduri R 2005 *Phys. Rev. B*, American Physical Society, **72** (12) 125206 doi: 10.1103/PhysRevB.72.125206

[22] Smith R 1992 *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* **67** (1) 335 doi: 10.1016/0168-583X(92)95829-G

[23] Sayed M, Jefferson J H, Walker A B and Cullis A G 1995 *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* **102** (1) 218 doi: 10.1016/0168-583X(95)80144-B

[24] Nordlund K, Nord J, Frantz J and Keinonen J 2000 *Computational Materials Science* **18** (3) 283 doi: 10.1016/S0927-0256(00)00107-5

[25] Moon W H and Hwang H J 2003 *Physics Letters A* **315** (3) 319 doi: 10.1016/S0375-9601(03)01039-9

[26] Goumri-Said S, Kanoun M B, Merad A E, Merad G and Aourag H 2004 *Chemical Physics* **302** (1) 135 doi: 10.1016/j.chemphys.2004.03.030

[27] Powell D, Migliorato M A and Cullis A G 2007 *Phys. Rev. B*, American Physical Society, **75** (11) 115202 doi: 10.1103/PhysRevB.75.115202

[28] Winczewski S, Shaheen M Y and Rybicki J 2018 *Carbon* **126** (Supplement C) 165 doi: 10.1016/j.carbon.2017.10.002

[29] Powell D 2006 *Elasticity, Lattice Dynamics and Parameterisation Techniques for the Tersoff Potential Applied to Elemental and Type III-V Semiconductors*, University of Sheffield

[30] McIntosh, Douglas F. 2010 *Theoretical Chemistry Accounts* **125** (3) 177 doi: 10.1007/s00214-009-0575-3

[31] Hardy R J 1982 *The Journal of Chemical Physics* **76** (1) 622 doi: 10.1063/1.442714

[32] Murdoch A I 1983 *Q. J. Mech. Appl. Math.* **36** 163

[33] Winczewski S, Dziedzic J and Rybicki J 2016 *Modelling and Simulation in Materials Science and Engineering* **24** (7) 75003

[34] Zhen Y and Chu Ch 2012 *Computer Physics Communications* **183** (2) 261 doi: 10.1016/j.cpc.2011.09.006

[35] Admal N C and Tadmor E B 2010 *Journal of Elasticity*, Springer Netherlands, **100** (1-2) 63 doi: 10.1007/s10659-010-9249-6

[36] Admal N C and Tadmor E B 2011 *The Journal of Chemical Physics* **134** (18) 184106 doi: 10.1063/1.3582905

[37] Yang J Z, Wu X and Li X 2012 *The Journal of Chemical Physics* **137** (13) 134104 doi: 10.1063/1.4755946

[38] Chen Y 2006 *The Journal of Chemical Physics* **124** (5) 54113 doi: 10.1063/1.2166387

[39] Fu Y and J-H Song 2014 *The Journal of Chemical Physics* **141** (5) 54108 doi: 10.1063/1.4891606

[40] Vanegas J M, Torres-Sánchez A and Arroyo M 2014 *Journal of Chemical Theory and Computation* **10** (2) 691